

COMPOUND FORMED FROM PRECIPITATED SILICA AND PHOSPHATE,
AND ITS USE AS A LIQUID SUPPORT WITH NUTRITIONAL
PROPERTIES AND AS AN ANTICAKING AGENT WITH NUTRITIONAL
PROPERTIES

5 The present invention relates to novel
compounds based on precipitated silica and phosphate,
in particular calcium phosphate, for use as a support
for a liquid, in particular a liquid animal feedstuff
complement, and preferably simultaneously as a
10 nutritional additive, in particular for animals.

It also relates to compositions comprising a
liquid, in particular a liquid animal feedstuff
complement, absorbed on a support formed by said novel
compound based on precipitated silica and phosphate.

15 Finally, the present invention also relates
to the use of said compounds, preferably after milling,
as an anticaking agent, a liquid atomization processing
aid, a solid milling or pelletization/tabletting
processing aid, and preferably simultaneously as a
20 nutritional additive for animals.

It is known for liquids, more particularly
animal feedstuff additives, to be conditioned on solid
supports, in particular on a silica support. Said
conditioning is generally aimed at transforming a
25 liquid that cannot be handled or is difficult to handle
into a fluid powder that can easily be stored, for

example in sacks or loose, which is easier to handle and which also can readily be dispersed and mixed with other divided solid constituents.

In the following text, the term "conditioned
5 composition" means the composition obtained, i.e. a liquid absorbed on a silica support.

Said conditioned composition must be capable of being handled easily, which implies good fluidity and low powdering, and hence the support has to be
10 mechanically strong and have good resistance to wear. It also has to have a relatively high active material (liquid) content and hence the support has to have a high absorption capacity and also a relatively high density. Those different requirements are sometimes
15 contradictory and are not necessarily satisfied by prior art silica supports.

The aim of the invention is to provide novel compounds constituting an alternative to known silica supports and which are particularly suitable for
20 conditioning liquids, especially liquid animal feedstuff complements.

To this end, in one aspect the invention provides a compound (or mixture) that can be obtained by spray drying a suspension hereinafter designated S
25 containing a precipitated silica and a phosphate selected from phosphates of elements from groups Ia or IIa of the periodic table of the elements and rare

earth phosphates.

Whether the precipitated silica is used as is in its solid form or in the form of an aqueous suspension obtained by re-dispersing the precipitated silica in the solid form in water, the precipitated
5 silica is very advantageously employed in the form of a filter cake or a suspension directly from its preparation process (precipitation reaction).

To this end, the present invention also
10 proposes a compound (or mixture) formed from precipitated silica and at least one phosphate selected from phosphates of elements from groups Ia or IIa of the periodic table of the elements and rare earth phosphates.

15 In accordance with the invention, drying is carried out by atomization (co-atomization), i.e. by spraying the suspension S into a hot atmosphere (spray drying). The compound (or mixture) of the invention can be termed a "co-atomizate". Drying is
20 advantageously carried out using an atomizing nozzle, for example monofluid or pressurized liquid. The temperature at the outlet from the atomizer is normally less than 170°C, in particular less than 140°C; as an example, it is in the range 100°C to 135°C.

25 Preferably, immediately prior to drying, the dry matter content of the suspension S is in the range 16% to 24% by weight, in particular in the range 18% to

24% by weight, for example in the range 18% to 22% by weight.

In a variation of the invention, the suspension S is obtained by mixing two precursors of a phosphate selected from phosphates of elements from groups Ia or IIa of the periodic table of the elements and rare earth phosphates with a suspension of precipitated silica. The term "two precursors" of a phosphate means a precursor providing the phosphate "portion" per se selected, for example, from orthophosphoric acid H_3PO_4 and its salts with formulae $\text{NH}_4\text{H}_2\text{PO}_4$, NaH_2PO_4 , KH_2PO_4 , $(\text{NH}_4)_2\text{HPO}_4$, and a precursor providing the element from group Ia or group IIa of the periodic table of the elements or rare earth "portion" selected in the case of calcium, for example, from lime $\text{Ca}(\text{OH})_2$, calcium nitrate $\text{Ca}(\text{NO}_3)_2$ and calcium chloride CaCl_2 .

In general, in this variation, the two phosphate precursors are added to the suspension of precipitated silica, usually with agitation, each in the solid form (i.e. the dry form, in particular a powder) or, as is preferable, in the form of an aqueous solution (which includes the case in which one is added in the solid form and the other is added in the form of a solution), under conditions such that said phosphate selected from phosphates of elements from groups Ia or IIa of the periodic table of the elements and rare

earth phosphates, is formed. The two precursors of said phosphate can be added simultaneously to the suspension of precipitated silica; preferably, they are added successively, the precursor providing the
5 phosphate "portion" per se being added first.

The mixture obtained can optionally undergo a disintegration operation, which can if necessary reduce the viscosity of the suspension to be dried subsequently. The disintegration operation can in
10 particular be carried out by passing the mixture into a mill, in particular of the colloidal or ball type or, as is preferable, into a high shear agitator, for example in the presence of water. It should be noted that the disintegration operation may coincide with the
15 mixing operation.

Mixing and optional disintegration are generally carried out at a temperature in the range 15°C to 70°C, for example in the range 20°C to 50°C.

In this variation, the suspension of
20 precipitated silica initially used may be directly from a process for preparing precipitated silica or may be obtained by disintegrating a filter cake from said preparation process (precipitation reaction). Said precipitated silica suspension generally has a dry
25 matter content in the range 16% to 24% by weight, in particular in the range 18% to 24% by weight, for example in the range 18% to 22% by weight.

In a further variation of the invention, the suspension S is obtained by mixing, generally with agitation, either a precipitated silica constituted by a filter cake from the reaction for precipitating said silica, or a suspension of precipitated silica, preferably obtained by disintegrating a filter cake from the reaction for precipitating said silica, with a phosphate selected from phosphates of elements from groups Ia or IIa of the periodic table of the elements and rare earth phosphates.

The filter cake disintegration operation can more particularly reduce its viscosity and can in particular be carried out by passing the cake through a high shear mixer or a mill, in particular of the colloidal or ball type, for example in the presence of water, and preferably in the presence of an aluminium compound, in particular sodium aluminate.

Similarly, the mixture obtained formed either from precipitated silica constituted by the filter cake or from the precipitated silica suspension and from the phosphate can optionally undergo a disintegration operation, which can reduce its viscosity if necessary.

The disintegration operation can in particular be carried out by passing the mixture through a mill, in particular a colloidal or ball type mill or, as is preferable, through a high shear mixer, for example in the presence of water. It should be noted that the

disintegration operation may coincide with the mixing operation. When precipitated silica constituted by a filter cake is used, a disintegration operation is generally carried out.

5 Mixing and optional disintegration are generally carried out at a temperature in the range 15°C to 70°C, for example in the range 20°C to 50°C.

4 The phosphate can be used in the form of an aqueous suspension or in the solid form, (for example
10 granules or, as is preferable, as a powder), with water optionally also being added to the precipitated silica suspension, generally with agitation.

 In this variation, the possible suspension of the precipitated silica used initially generally has a
15 dry matter content in the range 16% to 24% by weight, in particular in the range 18% to 24% by weight, for example in the range 18% to 22% by weight.

 Finally, although not constituting a preferred variation of the invention, the suspension S
20 can optionally be obtained by mixing precipitated silica in the solid form with a solution of a phosphate selected from phosphates of elements from groups Ia or IIa of the periodic table of the elements and rare earth phosphates.

25 The precipitated silica, in particular in the form of a suspension or a filter cake, used in accordance with the invention, is preferably prepared

by a process of the type comprising reacting a silicate with an acidifying agent then carrying out an optional separation operation (liquid-solid separation), the silica precipitation being carried out as follows:

- 5 (1) forming an initial stock comprising
at least a portion of the total quantity
of silicate engaged in the reaction and
in general at least one electrolyte, the
concentration of silicate (expressed as
10 SiO_2) in said initial stock being less
than 100 g/l, in particular less than 90
g/l, and the concentration of
electrolyte (for example sodium
sulphate) in said initial stock being
15 less than 17 g/l, for example less than
14 g/l;

(2) adding acidifying agent to said
stock to obtain a pH in the reaction
medium of at least about 7, generally in
20 the range about 7 to 8;

(3) adding acidifying agent to the
reaction medium simultaneously with the
remaining quantity of silicate, if
appropriate.

25 It should be noted that in general, the
process concerned is a process for synthesizing a
precipitated silica, i.e. an acidifying agent is caused

to act on a silicate under particular conditions.

The choice of acidifying agent and silicate are made in a manner that is known per se.

Generally, the acidifying agent used is a
5 strong mineral acid such as sulphuric acid, nitric acid
or hydrochloric acid, or an organic acid such as acetic
acid, formic acid or carbonic acid.

The acidifying agent can be dilute or
concentrated; its normality can be in the range 0.4 to
10 36 N, for example in the range 0.6 to 1.5 N.

Particularly in the case in which the
acidifying agent is sulphuric acid, its concentration
can be in the range 40 to 180 g/l, for example in the
range 60 to 130 g/l.

15 It is also possible to use as the silicate
any normal form of silicate such as metasilicates,
disilicates or, advantageously, an alkali metal
silicate, in particular sodium or potassium silicate.

The silicate can have a concentration
20 (expressed as SiO_2) in the range 40 to 330 g/l, for
example in the range 60 to 300 g/l, in particular in
the range 60 to 260 g/l.

In general, the acidifying agent used is
sulphuric acid and the silicate is sodium silicate.
25 When using sodium silicate, it generally has a $\text{SiO}_2/\text{Na}_2\text{O}$
weight ratio in the range 2 to 4, for example in the
range 3.0 to 3.8.

The initial stock generally comprises an electrolyte. The term "electrolyte" as used here has its normal meaning, i.e. it means any ionic or molecular substance which, when in solution, decomposes or dissociates to form ions or charged particles. Electrolytes which can be cited include salts from the alkali and alkaline-earth metal salt group, more particularly the salt of the starting metal silicate and the acidifying agent, for example sodium chloride when reacting a sodium silicate with hydrochloric acid or, as is preferable, sodium sulphate when reacting a sodium silicate with sulphuric acid.

In the (preferred) case in which the starting stock comprises only a portion of the total quantity of silicate engaged in the reaction, the acidifying agent and the remaining quantity of silicate are simultaneously added in step (3).

Said simultaneous addition is preferably carried out in a manner that keeps the pH to a value that is equal to (± 0.2) the value at the end of step (2).

In general, in a subsequent step, a supplemental quantity of acidifying agent is added to the reaction medium until the pH of the reaction medium is in the range 3 to 6.5, in particular in the range 4 to 6.5.

It may then be advantageous to mature the

reaction medium, following said addition of a supplemental quantity of acidifying agent, said maturing taking 2 to 60 minutes, in particular 3 to 20 minutes, for example.

5 When the starting stock comprises the total quantity of the silicate used in the reaction, in step (3), the acidifying agent is added, preferably until the pH of the reaction medium reaches a value in the range 3 to 6.5, in particular in the range 4 to 6.5.

10 It may then be advantageous to mature the reaction medium following said step (3), said maturing taking 2 to 60 minutes, more particularly 3 to 20 minutes, for example.

15 The reaction chamber in which the complete reaction of the silicate with the acidifying agent is carried out is normally provided with suitable agitation equipment and heating equipment.

20 The complete reaction of the silicate with the acidifying agent is generally carried out between 70°C and 98°C.

 In a variation of the process, the complete reaction of the silicate with the acidifying agent is carried out at a constant temperature, preferably in the range 80°C to 95°C.

25 In a (preferred) variation of the process, the temperature at the end of the reaction is higher than the temperature at the start of the reaction:

thus, the temperature at the start of the reaction is preferably kept between 70°C and 95°C, then the temperature is increased, preferably to a value in the range 80°C to 98°C, and it is kept at that value until
5 the end of the reaction.

On completion of the steps described above, a slurry/suspension of silica is obtained, which can then undergo a liquid-solid separation operation.

In general, said separation comprises
10 filtering and washing using a filter provided with compacting means.

Said filter can be a band filter provided with a roller for compacting.

However, said filter is preferably a filter
15 press; separation then generally comprises filtering, washing then compacting using said filter.

The phosphate employed in the context of the invention is selected from phosphates of elements from groups Ia or IIa of the periodic table of the elements
20 and rare earth phosphates.

It is generally selected from phosphates of sodium, potassium, calcium, magnesium and rare earths (more particularly cerium, lanthanum). Preferably, said phosphate is a calcium phosphate, in particular a
25 monocalcium phosphate (MCP) also known as calcium dihydrogen phosphate with formula $\text{Ca}(\text{H}_2\text{PO}_4)_2$, dicalcium phosphate (DCP) also known as calcium hydrogen

phosphate CaHPO_4 , or a tricalcium phosphate (TCP) also known as hydroxyapatite; highly preferably, a monocalcium phosphate (MCP) or a dicalcium phosphate (DCP) is used.

5 The phosphates used generally have a median particle size d_{50} of less than 100 μm , in particular less than 50 μm , and more particularly less than 25 μm .

 The compounds of the invention can optionally undergo a subsequent heat treatment.

10 In the following description, the tamped packing density (TPD) and the non tamped packing density (NPD) were determined in accordance with French standard NF T 30-042.

 The DOP oil uptake was measured in accordance
15 with NF T 30-022 (March 1953) using dioctylphthalate.

 The pore volumes given were measured by mercury porosimetry; each sample was prepared as follows: each sample was initially oven dried for 2 hours at 200°C, then placed in a test receptacle during
20 the 5 minutes following withdrawal from the oven and then vacuum degassed, for example using a rotary vane pump; the pore diameters (MICROMERITICS Autopore III 9420 porosimeter) were calculated using the WASHBURN relationship with a contact angle θ of 140° and a
25 surface tension γ of 484 dynes/cm (or N/m).

 The BET specific surface area was determined using the BRUNAUER-EMMET-TELLER method described in the

"Journal of the American Chemical Society", vol. 60, page 309, February 1938 and corresponded to International standard ISO 5794/1 (annex D).

The CTAB specific surface area was the
5 external surface area determined in accordance with French standard NF T 45007 (November 1987) (5.12).

The Carr index (Ci) of the compounds of the invention, which illustrates their fluidity (flowability), was determined using the following
10 relationship: $Ci = (TPD - NPD) / TPD$.

The wear resistance of the compounds of the invention was determined as follows: it was expressed as the percentage of particles in a 100 μm - 200 μm cut obtained by sieving remaining after wear lasting 2
15 minutes (wear resistance designated R_{wr2}), 5 minutes (wear resistance designated R_{wr5}), and 10 minutes (wear resistance designated R_{wr10}), on a 50 μm vibrating sieve in the presence of 50 glass beads with a diameter of 4 mm, the initial mass of the sample particles
20 initially disposed on the vibrating sieve being 1 gram. During the wear procedure, the sieve was vibrated using a RETSCH VE 1000 vibrating table used with a 2 mm amplitude.

The median diameter d_{50} (by weight) was
25 determined using a MALVERN Mastersizer 2000 and its Hydro 2000G suspension sampler.

The compounds (or mixtures) of the invention

generally have an amount of phosphate, selected from phosphates of elements from groups Ia or IIa of the periodic table of the elements and rare earth phosphates, of at least 10% by weight, preferably at least 20% by weight (dry weight). Advantageously, their phosphate content is in the range 20% to 60% by weight, in particular in the range 20% to 50% by weight. In particular, it can be between 20% and 40% by weight, for example between 20% and 35% by weight.

The compounds of the invention are advantageously in a particular form, namely in the form of substantially spherical beads with a median diameter d_{50} which is generally at least 80 μm , preferably at least 100 μm ; said diameter is, for example, in the range 100 μm to 400 μm , more particularly in the range 110 μm to 300 μm and in particular in the range 130 μm and 280 μm . Said beads generally have a sphericity factor (defined as indicated in International patent application WO-A-98/35751, a value of 1 corresponding to a perfect sphere) of at least 0.900, in particular at least 0.920, for example at least 0.940. Their sphericity factor can be at least 0.960. Preferably, said beads are solid (i.e. not hollow) and are not powdery, i.e. generate little or no dust especially during handling.

The compounds of the invention advantageously have good mechanical resistance/cohesion in particular

good wear resistance, which ensures their non powdery character especially during handling and also a porosity that provides them with a high absorbing power.

5 In general, they thus have:

- a wear resistance R_{wr2} of at least 60%, in particular at least 80%, more particularly at least 82%; and/or
- a wear resistance R_{wr5} of at least 50%,
10 in particular at least 55%; and/or
- a wear resistance R_{wr10} of at least 15% in particular at least 17%.

Their DOP oil uptake is normally more than 170 ml/100g, more particularly more than 210 ml/100g.

15 It may be at least 230 ml/100g, for example at least 240 ml/100g.

The compounds of the invention advantageously have a DOP oil uptake that is higher than the DOP oil uptake of the composition obtained by dry mixing said
20 precipitated silica in the solid form with said phosphate in the solid form.

Their pore volume (V_{d1}) constituted by pores with a diameter of less than 1 μm can be at least 1.2 cm^3/g , in particular at least 1.3 cm^3/g , more
25 particularly at least 1.4 cm^3/g ; as an example, it can be at least 1.5 cm^3/g . It is generally less than 2.2 cm^3/g , for example 1.8 cm^3/g .

The compounds of the invention have a fairly high density, more particularly higher than that of the precipitated silica they contain; their tamped packing density (TPD) is preferably more than 0.29, in particular at least 0.30. It can be at least 0.31, for example at least 0.33.

Their PET specific surface area is generally in the range 60 m²/g to 250 m²/g, in particular in the range 90 m²/g to 200 m²/g, for example in the range 100 m²/g to 160 m²/g.

They have very good fluidity (flowability), which in general is improved over that of the precipitated silica they contain. They may have a Carr index (Ci) of less than 0.1.

The Applicant has discovered that the compounds (or mixtures) defined above advantageously have a high absorption capacity, improved fluidity and good mechanical resistance/cohesion, in particular good wear resistance, resulting in a non powdery character, especially during handling, and are particularly suitable for conditioning liquids.

In further aspects, the invention pertains to the use of a compound as described above as a support for a liquid and to a conditioned composition comprising at least one liquid absorbed on a support formed by a compound as defined above.

Liquids that can be cited are organic liquids

such as organic acids, surfactants, for example of the anionic or non-ionic type, organic additives for rubber/polymers, or pesticides.

However, particular examples of liquids that
5 can be used here are liquid additives such as:
preservatives (more particularly phosphoric acid, propionic acid), flavours, colorants, liquid foodstuff complements.

The compounds described above are
10 particularly suitable for conditioning liquid foodstuff complements, more particularly liquid animal foodstuff complements. Examples that can be cited are choline, choline hydrochloride, vitamins such as vitamins A, B, C, D, K, and, preferably, vitamin E (or its acetate).

15 One essential advantage of the present invention resides in the fact that in addition to their use as a support for a liquid additive, in particular for a liquid animal foodstuff complement, the compounds of the invention have a nutritional value, or even a
20 therapeutic value and can be used simultaneously as a nutritional or even a therapeutic additive for animals, thus encouraging the growth and health of animals, more particularly breeding animals.

The present invention associates, in one and
25 the same product, a nutritional additive or even a therapeutic additive such as calcium phosphate with a liquid additive, more particularly a liquid foodstuff

complement, in particular animal foodstuff, such as vitamin E (or its acetate), for example.

The operation for absorbing liquid onto the support formed by the compound of the invention can be carried out conventionally, in particular by spraying the liquid onto the support in a mixer.

The conditioned composition of the invention can, more particularly in the case of vitamin E (or its acetate), have a liquid content of at least 50% by weight, in particular in the range 50% to 70%, for example in the range 50% to 65% by weight; the liquid content can be at least 52% by weight. This high liquid content illustrates the high absorbing power with which the compounds of the invention are preferentially endowed. Even higher liquid contents can be employed, in particular in the case of choline hydrochloride.

It should be noted that the compounds of the invention can permit more rapid and/or easier release of a liquid, more particularly of vitamin E (or its acetate) into its medium of use, for example the body of an animal.

Because of the presence of the compound described above, the conditioned compositions of the invention preferably exhibit little or no dust formation and very good fluidity (flowability), combined with a rather high density.

The present invention also pertains to the use of the compounds of the invention as an anticaking agent; preferably, said compounds are milled prior to said use, for example to a particle size in the range
5 1 μm to 100 μm , more particularly in the range 2 μm to 50 μm . They can be used as an anticaking agent in human foodstuffs, for example fishes, cheeses, sugar, polydextrose, flavours, dried fruits, coffee powder, tea, cocoa, in animal foodstuffs, for example
10 formulations, feeds, and also in agriculture, in the detergent industry, in the pharmacy, in cosmetics and in a variety of industrial applications (such as rubber/polymers, toners, fire extinguisher powder, concrete, latex powder).

15 It also concerns their use as a liquid atomization processing aid, as a solid milling processing aid, and in particular in the detergent industry and in the pharmacy as a pelletization and/or tabletting aid; preferably, said compounds are milled
20 prior to said use, for example to a particle size in the range 1 μm to 100 μm , in particular in the range 2 μm to 50 μm .

When used as a liquid atomization aid, when added to the liquid that is to be dried by atomization,
25 it prevents adhesion to the walls of the atomizer and also produces a non-caked final powder with good flowability (possible application: the dairy fattening

industry).

When used as a powder milling aid, when added to a powder in a mill, it improves milling of said powder and also produces a final non-caked powder with good flowability (possible application: polymer industry).

When used as an anticaking agent, preferably after milling, a liquid atomization processing aid, as a processing aid for milling a solid or for pelletization/tabletting, the compounds of the invention have the major advantage of having a nutritional value and of being able to be used simultaneously as a nutritional additive, more particularly for animals.

The following examples illustrate the invention without in any way limiting the invention.

EXAMPLE 1

1) The following were introduced into a stainless steel reactor provided with a propeller agitator system and jacket heating system:

- 345 litres of water;
- 7.5 kg of Na_2SO_4 ;
- 588 litres of aqueous sodium silicate with a $\text{SiO}_2/\text{Na}_2\text{O}$ weight ratio of 3.5 and a density at 20°C of 1.133.

The silicate concentration, expressed as SiO_2 , in the initial stock was thus 85 g/l. The mixture was

heated to a temperature of 82°C, maintaining agitation. 387 litres of dilute sulphuric acid with a density at 20°C of 1.050 was introduced to obtain in the reaction medium a pH (measured at its temperature) of 8.0. The
5 reaction temperature was 82°C for the first 25 minutes; it was then heated from 82°C to 92°C over 15 minutes, then kept at 92°C until the end of the reaction.

82 litres of aqueous sodium silicate of the type described above and 134 litres of sulphuric acid,
10 also of the type described above, were then introduced (i.e. when the pH of the reaction medium had reached 8.0) together into the reaction medium, said simultaneous introduction of acid and silicate being carried out in a manner such that the pH of the
15 reaction medium during the introduction period was kept at 8.0 ± 0.1 . After introducing all of the silicate, dilute acid introduction was continued for 9 minutes to bring the pH of the reaction medium to 5.2. After said acid introduction, the reaction slurry obtained was
20 agitated for 5 minutes.

The total reaction period was 118 minutes.

A slurry or suspension of precipitated silica was obtained, which was then filtered and washed using a vertical plate filter press (said plates being
25 provided with deformable membranes which could compress the filter cake by introducing pressurized air), at a pressure of 4.5 bars and for the time required to

obtain a cake of silica with a loss on ignition of 80.5% (and thus a dry matter content of 19.5% by weight).

The cake obtained was then fluidized by mechanical and chemical action (adding a quantity of sodium aluminate corresponding to a Al/SiO₂ weight ratio of 3000 ppm); during said operation, water was added to obtain a slurry with a loss on ignition of 81.0% (and thus a dry matter content of 19.0% by weight). After this disintegration operation, the resulting suspension R, with a pH of 6.4, was dried using a monofluid nozzle atomizer.

The precipitated silica obtained was in the form of substantially spherical beads and had the following characteristics:

- BET specific surface area 159 m²/g
- Median diameter d₅₀ 174 μm
- DOP oil uptake 296 ml/100g
- Pore volume (V_{d1}) 2.0 cm³/g
constituted by pores with d < 1 μm
- TPD 0.27
- NPD 0.24
- Carr index Ci 0.111
- Wear resistance
 - R_{wr2} 83%
 - R_{wr5} 56%
 - R_{wr10} 18%

2) Vitamin E acetate was placed on the support formed by the silica prepared in 1).

The vitamin E acetate was supported in a 7

litre Patterson Kelley V mixer rotating at 20 rpm with an internal axis rotating at 1900 rpm provided with plates through which the vitamin E acetate was sprayed and on which lump breaking knives were mounted.

5 800 g of the silica prepared in 1) was charged into the mixer, then 978 g of vitamin E acetate was sprayed at a temperature of 80°C for 10 minutes over said silica. Agitation in the homogenizer was maintained for 5 more minutes.

10 The conditioned composition obtained contained 45% by weight of precipitated silica and 55% by weight of vitamin E acetate and had the following supplemental characteristics:

- TPD 0.58
- NPD 0.53
- Carr index Ci 0.086

15

EXAMPLE 2

1) 156 kg of a suspension of precipitated silica R as prepared in 1) with a dry matter content of 19.0% by weight was charged into a 300 litre stainless steel tank provided with a blade agitator. Said
20 suspension was pumped and sent through a circuit to a 60 litre reactor provided with a triple blade agitator. 10 kg of monocalcium phosphate powder (i.e. 25% by weight of calcium phosphate with respect to the dry weight of calcium phosphate + silica) sold under
25 the trade name IBEX* MCP by Rhodia Consumer

Specialities was added to said suspension in the reactor (which was at a temperature of about 20°C) using a worm dosimeter, along with 40 kg of water; the introduction period was about 1 hour. The resulting suspension was then dried using a monofluid nozzle atomizer.

The compound obtained, formed from precipitated silica and calcium phosphate, was in the form of substantially spherical beads and had the

10 following characteristics:

- BET specific surface area 103 m²/g
- Median diameter d₅₀ 136 μm
- DOP oil uptake 241 ml/100g
- Pore volume (V_{d1}) 1.7 cm³/g
constituted by pores with d < 1 μm.
- TPD 0.33
- NPD 0.30
- Carr index Ci 0.091
- Wear resistance
 - R_{wr2} 84%
 - R_{wr5} 57%
 - R_{wr10} 25%

This compound of the invention was thus denser than the precipitated silica obtained in Example

1. Its fluidity was also improved (lower Carr index) and its wear resistance was better, all the while having nutritional properties.

2) Vitamin E acetate was placed on the support formed by the compound (mixed silica-phosphate)

prepared in 1).

The vitamin E acetate was supported in a 7 litre Patterson Kelley V mixer rotating at 20 rpm with an internal axis rotating at 1900 rpm provided with
5 plates through which the vitamin E acetate was sprayed and on which lump breaking knives were mounted.

1000 g of the compound prepared in 1) was charged into the mixer, then 1222 g of vitamin E acetate was sprayed at a temperature of 80°C for 10
10 minutes over said compound. Agitation in the homogenizer was maintained for 5 more minutes.

The conditioned composition obtained contained 45% by weight of precipitated silica and 55% by weight of vitamin E acetate and had the following
15 supplemental characteristics:

- TPD 0.71
- NPD 0.65
- Carr index Ci 0.084

This conditioned composition, based on a mixed silica-phosphate support in the form of substantially spherical beads, had good fluidity, as illustrated by the low Carr index, said fluidity even
20 being improved over that of the conditioned composition prepared in Example 1. Its density was also higher.

EXAMPLE 3

1) 156 kg of a suspension of precipitated silica R as prepared in 1) with a dry matter content of
25 19.0% by weight was charged into a 300 litre stainless

steel tank provided with a blade agitator. Said suspension was pumped and sent through a circuit to a 60 litre reactor provided with a triple blade agitator.

9.9 kg of tricalcium phosphate powder (i.e. 25% by weight of calcium phosphate with respect to the dry weight of calcium phosphate + silica) sold under the trade name TCP 118 FG by Rhodia Consumer Specialities was added to said suspension in the reactor (which was at a temperature of about 20°C) using a worm dosimeter, along with 41 kg of water; the introduction period was about 1 hour. The resulting suspension was then dried using a monofluid nozzle atomizer.

The compound obtained, formed from precipitated silica and calcium phosphate, was in the form of substantially spherical beads and had the following characteristics:

- BET specific surface area 129 m²/g
- Median diameter d₅₀ 154 µm
- DOP oil uptake 252 ml/100g
- Pore volume (V_{d1}) 1.6 cm³/g
constituted by pores with d < 1 µm
- TPD 0.31
- NPD 0.28
- Carr index Ci 0.097
- Wear resistance
 - R_{wr2} 84%
 - R_{wr5} 56%
 - R_{wr10} 19%

This compound of the invention was thus

denser than the precipitated silica obtained in Example 1. Its fluidity was also improved (lower Carr index) and its wear resistance was better, all the while having nutritional properties.

5 2) Vitamin E acetate was placed on the support formed by the compound (mixed silica-phosphate) prepared in 1).

The vitamin E acetate was supported in a 7 litre Patterson Kelley V mixer rotating at 20 rpm with
10 an internal axis rotating at 1900 rpm provided with plates through which the vitamin E acetate was sprayed and on which lump breaking knives were mounted.

900 g of the silica prepared in 1) was charged into the mixer, then 1100 g of vitamin E
15 acetate was sprayed at a temperature of 80°C for 10 minutes over said silica. Agitation in the homogenizer was maintained for 5 more minutes.

The conditioned composition obtained contained 45% by weight of mixed silica-phosphate and
20 55% by weight of vitamin E acetate and had the following supplemental characteristics:

- | | |
|-----------------|--------|
| • TPD | 0.70 |
| • NPD | 0.64 |
| • Carr index Ci | 0.0857 |

This conditioned composition based on a mixed silica-phosphate support in the form of substantially spherical beads had good fluidity, as illustrated by
25 the low Carr index. Its density was higher than that

of the conditioned composition prepared in Example 1.

EXAMPLE 4

1) 178 kg of a suspension of precipitated silica R as prepared in 1) with a dry matter content of 19.0% by weight was charged into a 300 litre stainless steel tank provided with a blade agitator. Said suspension was pumped and sent through a circuit to a 60 litre reactor provided with a triple blade agitator. 22.3 kg of tricalcium phosphate powder (i.e. 40% by weight of calcium phosphate with respect to the dry weight of calcium phosphate + silica) sold under the trade name TCP 118 FG by Rhodia Consumer Specialities was added to said suspension in the reactor (which was at a temperature of about 20°C) using a worm dosimeter, along with 41 kg of water; the introduction period was about 1 hour. The resulting suspension was then dried using a monofluid nozzle atomizer.

The compound obtained, formed from precipitated silica and calcium phosphate, was in the form of substantially spherical beads and had the following characteristics:

- BET specific surface area 112 m²/g
- Median diameter d₅₀ 144 μm
- DOP oil uptake 240 ml/100g
- Pore volume (V_{d1}) 1.5 cm³/g
constituted by pores
with d < 1 μm
- TPD 0.36
- NPD 0.33
- Carr index Ci 0.083
- Wear resistance

R _{wr2}	83%
R _{wr5}	55%
R _{wr10}	18%

This compound of the invention was thus denser than the precipitated silica obtained in Example 1. Its fluidity was also greatly improved (much lower Carr index) and its wear resistance was still

5 satisfactory, all the while having nutritional properties.